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CRLR 528
Project 4-92-03-012

FORMAL REPORT

THICKENING OF FS (U)

by

Sigmund R. Eckhaus
Edward J. Herbster

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CHEMICAL CORPS
CHEMICAL AND RADIOLOGICAL LABORATORIES
Army Chemical Center
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28 May 1956

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CRLR 528, 6 Apr 56, 14 pp - illus - tables (CONFIDENTIAL)
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CHEMICAL AND RADIOLOGICAL LABORATORIES
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CRLR 528
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FORMAL REPORT

THICKENING OF FS (U)

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APPROVED:

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ABSTRACT

Object.

The object of project 4-92-03-012 was to investigate, design, develop, and operate pilot plants for the production of CW agents.

The object of the work described in this report was to develop a process for thickening FS and to prepare sufficient material for field tests.

Results.

A process to thicken FS with ammonium sulfate was developed and operated. Two lots of thickened material were prepared.

Conclusions.

The process presented for thickening FS is satisfactory and can be scaled up, if the following important precautions are observed:

1. Use of only dry ammonium sulfate.
2. Use of an efficient exhaust scrubber.

Recommendations.

None, since immediate requirements for thickened FS were met.

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THICKENING OF FS (U)

I. INTRODUCTION.

A. Object.

The object of project 4-92-03-012 was to investigate, design, develop, and operate pilot plants for the production of CW agents.

The object of the work described in this report was to develop a process for thickening FS and to prepare sufficient material for field tests.

B. Authority.

Authority for this work was contained in the 1955 project program, Project 4-92-03-012, CW Agent Pilot Plants.

II. DEVELOPMENT OF PROBLEM.

The need of thickened FS became apparent in World War II, when it was desired to produce large smoke curtains (from 300 to 400 ft. altitudes) rather than smoke screens (50 to 100 ft.). Also, with faster planes, it was desirable to disseminate smoke screens from higher altitudes.

Ammonium sulfate was a satisfactory thickener for FS and also was the cheapest of the salts that were tried.

It was reported that no reduction in the amount of smoke resulted from the dissolution of up to 15% ammonium sulfate in FS. It was preferable, but not essential, to the ammonium sulfate thoroughly dry before mixing with FS. The drier the salt, the less heat was evolved. The production of heat was, however, not necessarily a disadvantage, as solution was thereby accelerated (1).

A viscosity of 50 to 100 centipoise at the temperature of spraying was estimated to be the optimum. At higher viscosities drops would become too large and thus settle too fast. A 5% to 9% ammonium sulfate concentration in FS was required to produce this viscosity. Data showing the relationship between the ammonium sulfate concentration and the viscosity of thickened FS at various temperatures (1, 2, 3) are shown in table 1 and plotted in fig. 1.

Table 1

Viscosity of Thickened FS

Ammonium sulfate	Viscosity	
	At 0°C.	At 25°C.
%	Cp.	Cp.
0	40.0	9.4
2.5	-	18.0
5.0	230.3	38.0
10.0	1,400.0	155.0

As a result of some work done in 1944, it was concluded, "At present, the use of thickened FS does not possess sufficient advantages over unthickened material to offset the difficulties of preparation" (4). This thickening was performed out of doors, directly in the FS drum. Much spattering, fumes, and smoke were produced. After several additions of the ammonium sulfate and much tedious drum rolling, samples were taken and the viscosity was determined. The process was repeated for every drum required. The procedure was long and hazardous, and variations of viscosities from drum to drum were excessive.

Because of the previous difficulties mentioned above and the requirement for thickened FS, the following process was developed.

In calculating the heat or cooling requirements of the system, a heat of solution of 45 kg.cal./mole was used for the ammonium sulfate-FS system (3). Thickened FS with viscosity of 115 centipoise at 25°C. was desired for field trials.

III. EXPERIMENTAL.

A. Materials and Equipment.

1. Materials.

a. FS mixture, Government Spec. JAN-C-379, approved 8 August 1946, 45% chlorosulfonic acid ($ClHSO_3$) and 55% sulfur trioxide (SO_3). The mixture was a brown liquid with a density of 1.90.

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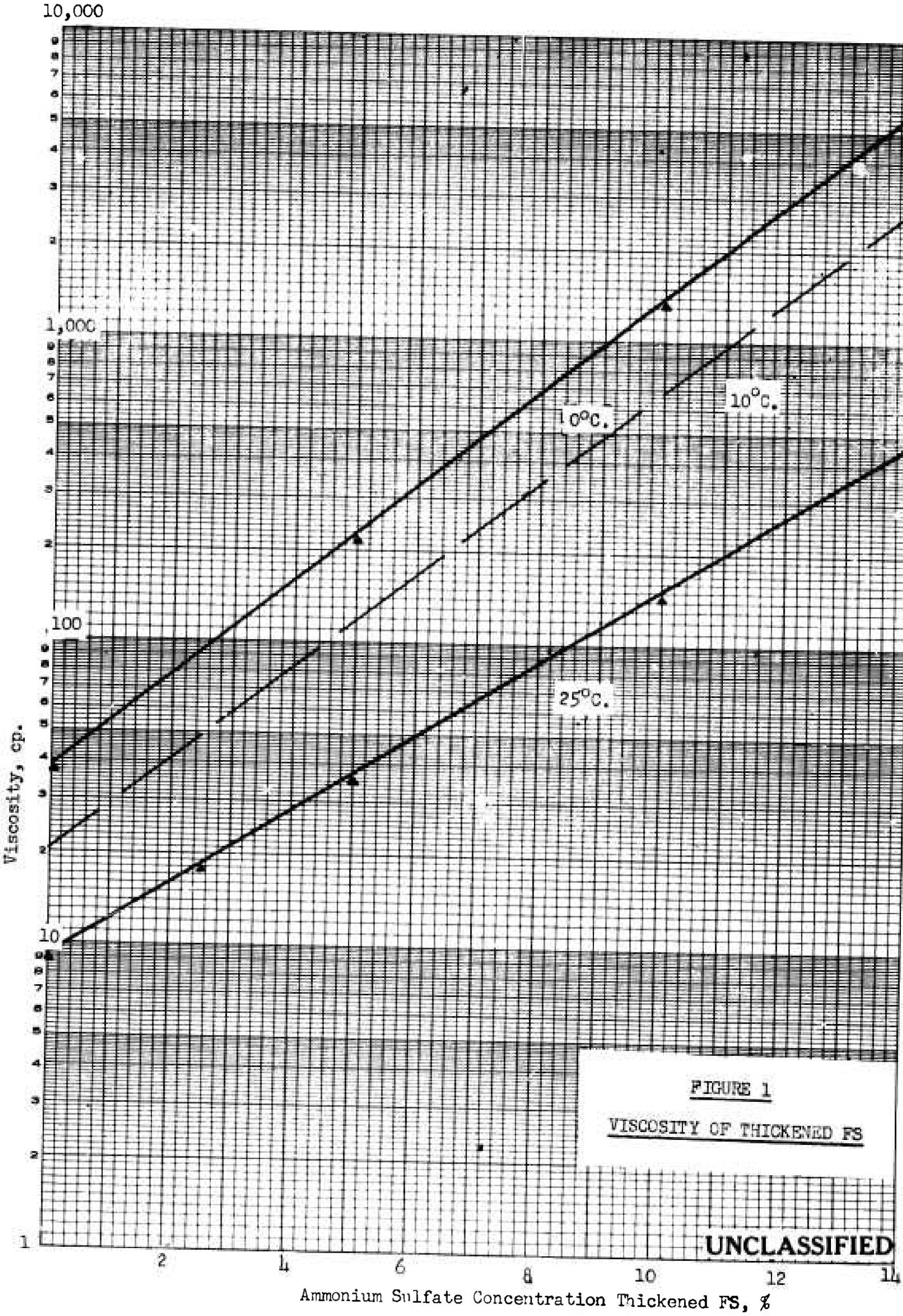

FIGURE 1

VISCOSITY OF THICKENED FS

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b. Ammonium sulfate ($(NH_4)_2SO_4$), c.p. grade. A white, purified, granular solid supplied by Mallinckrodt Chemical Company.

c. Dowtherm E. o-Dichlorobenzene, an oil, clean, yellowish liquid. It melts at -4°F. and boils at 496°F.

d. Water. As supplied from tap, suitable for drinking.

e. Drierite, calcium sulfate ($CaSO_4$). A hyroscopic material supplied by Hammond Drierite Company.

2. Equipment. (See fig. 2.)

a. 50-gal. Glass-lined jacketed Pfaudler reactor with a glass-lined head, glass-coated anchor-type agitator, and glass-coated thermometer well.

b. Iron cold finger, 1-1/2 in. by 6 ft., with a 3-in. by 5-ft. pyrex glass shell. Attached to 3-in. flanged opening on reactor.

c. Hopper with screw feed, a 1-in. brass spiral screw driven by a gear head motor turning at 57.5 r.p.m. The hopper was constructed of 16-gage sheet metal with a lucite top.

d. Dowtherm cooling system, which consisted of a six-tube, 5-ft. by 1/2-in. water-jacketed heat exchanger, a 1.3-h.p. Eastern model F circulating pump, a Fischer-Porter Ratio-sight flow indicator having a 10-gal./min. capacity, and an 18 by 3-in. pyrex head tank with necessary valves and piping.

e. A Minneapolis-Honeywell temperature indicator, scale range -80° to +160°C. divisions; accuracy 5%.

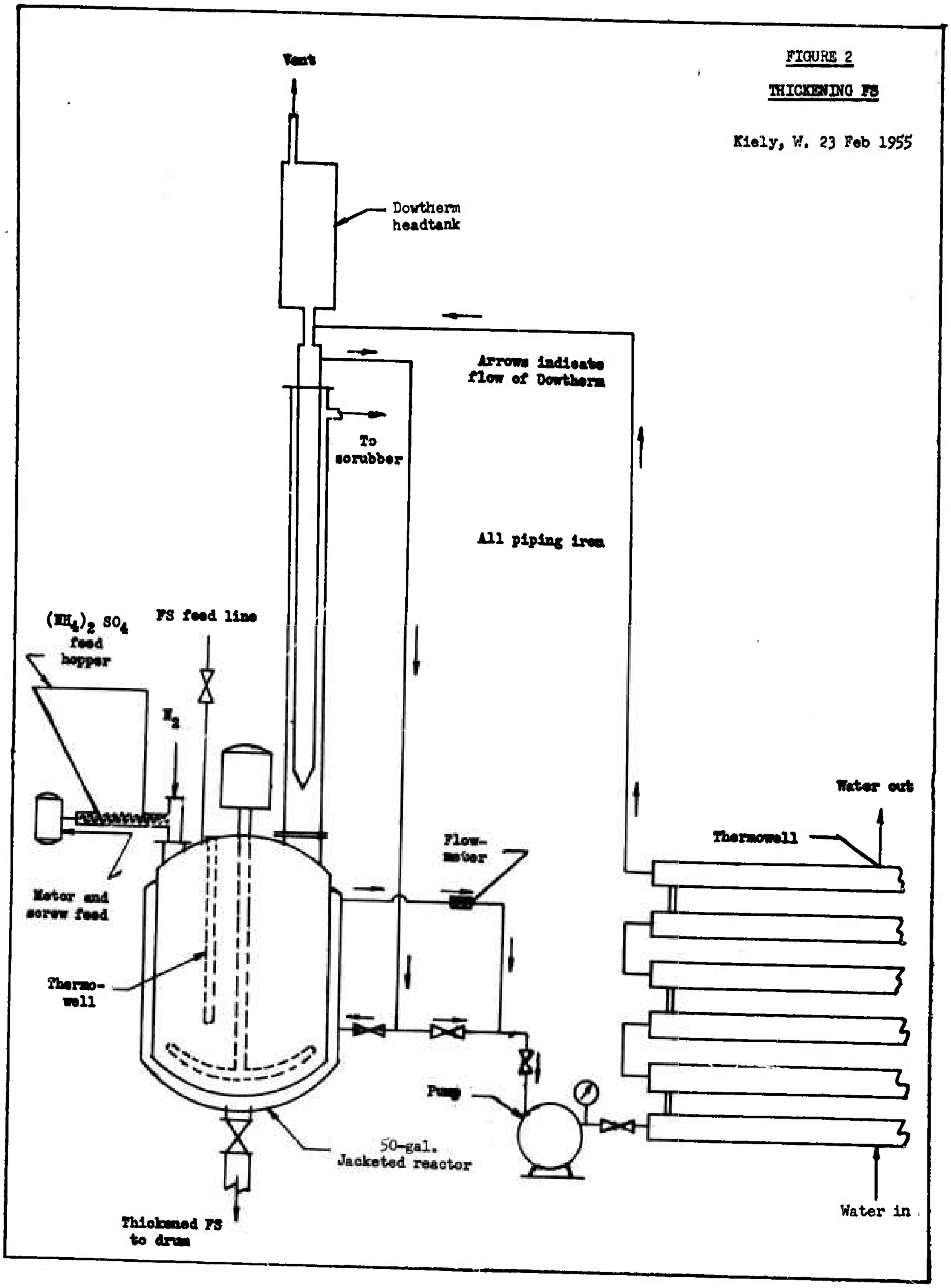
f. Ostwald-Fenske-Cannon viscometer, ASTM, calibrated.

g. FS feed to reactor, consisting of supply drum on scales with a flexible steel hose attached to drum and line to reactor. A 1-ft. by 2-in. pipe filled with Drierite was attached to the drum vent to dry the air entering drum.

h. Thickened-FS drum-loading system, consisting of pipeline from bottom of reactor leading to two drums on scales attached with flexible steel hose.

i. Scales, 1,000 lb., platform type, two each.

j. Rubber gloves, rubber aprons, rubber buckets, gas masks.



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B. Procedure.

1. Thickening FS.

The reactor was inspected to insure that it was clean and dry. The N_2 purge was started, the cooling water was turned on, and Dowtherm was circulated through the condenser. A 55-gal. drum of FS was placed on a scale on the floor above and connected to the feed line. A tube filled with Drierite was connected to the drum vent. The total contents of the drum were added at one time, the weight on the scale indicating when the drum was empty.

The amount of $(NH_4)_2SO_4$ to be added was weighed out and placed in the hopper during the operation as needed. The reactor agitator was started, and then the feed screw drive was started. The feed rate, manually regulated by varying the rheostat setting on the motor driving the screw, was dictated by the temperature of the exothermic FS-$(NH_4)_2SO_4$ reaction. When the temperature of the reaction rose to 35°, cold Dowtherm was circulated through the reactor jacket. Then the mixture temperature was allowed to rise to 50°C. and was held at that temperature by regulating the Dowtherm flow. A flowmeter was used to indicate this flow. After the desired amount of $(NH_4)_2SO_4$ had been added, the mixture was cooled during agitation to approx 25°C. The cooled mixture was dropped to two drums on the first floor. A single batch of thickened FS was split between two receiving drums. Two batches in two drums constituted a lot. Each drum was sampled after filling and rolling.

2. Analytical Procedure.

The viscosity of the thickened material was measured with an Ostwald-Fenske-Cannon ASTM viscometer. The sample was placed in the tube, and drying tubes filled with Drierite were placed over the openings. The material was pulled into the measuring bulk by applying suction through a drying tube. The ASTM method was employed to determine the viscosity. Three good checks were obtained on each sample, with temperature readings recorded at the start and the finish.

3. Safety Precautions.

The main hazard in this process occurs when handling the FS before and after the thickening process. When opening the FS drums, care was taken because of the rapid evolution of gas and smoke. Gas masks, rubber gloves, and rubber aprons were worn at this point. Sampling and determination of the viscosity were also done while wearing protective equipment. Any contact between FS and the skin would result in serious burns, and, therefore, maximum protection was provided.

C. Results.

Table 2 lists the results obtained from four batches of thickened FS prepared by this process. This material was placed in drums, sampled, labeled, and submitted for use in field test.

Table 2

Results of Thickening FS With 9% Ammonium Sulfate

Batch	FS		$(NH_4)_2SO_4$	Product			
	Lot	Weight		Drum	Amount delivered	Viscosity	
		lb.	lb.		lb.	cp.	°C.
1	1	726	72	T1-1	771	102	28
2	1	710	70	T1-2	760	97	29
3	2	738	73	T2-1	803	80	32
4	2	747	74	T2-2	823	80	32

IV. DISCUSSION.

A. Reproducibility.

A viscosity of 115 cp. at 25°C. was desired for the thickened material. In the temperature range studied (25° to 35°C.), the viscosity varied approx. 5 cp./°C. Using 5 cp./°C. and correcting all the viscosities to 25°C., the viscosity for each batch was 117, 117, 115, and 115 cp., respectively. These results were very satisfactory for field tests and far more reproducible than results reported previously (4). It was also found after several days in the drums that the viscosity had not changed more ± 5 cp. at this concentration.

The loss in weight of batches one and two was due to the presence of moisture (see B below). An effort was made in batches 3 and 4 to prevent the introduction of moisture, with a resulting decrease in loss of weight. The losses for batches 1 and 2 averaged 3.1%, while the losses for batches 3 and 4 were less than 1%.

B. Process Operations.

The highly exothermic reaction between FS and water necessitates special consideration of several process operations. The possible reactions between FS and water are given below:

a. $FS + H_2O \rightarrow HCl + SO_3$

b. $SO_3 + H_2O \rightarrow H_2SO_4$

The ammonium sulfate used contained traces of water, and it also picked up moisture from the atmosphere. This moisture content caused the salt to cake and bridge in the feed hopper, necessitating periodic breaking up the salt in the hopper. The screw feed and inlet to the reactor on several occasions became plugged with salt and had to be cleaned out. The use of dry ammonium sulfate and a method of keeping it dry would eliminate this difficulty.

A nitrogen flow was used to purge the system to provide a moisture-free atmosphere. It was applied at the salt-feed inlet, and helped prevent caking to some extent.

Dowtherm was used as the cooling medium for the equipment because the direct use of water was considered hazardous. If a leak should develop in the cold finger or in the reactor jacket, the resulting reaction between FS and water would be explosive.

The system was vented into an existing caustic scrubber, but the fumes during the reaction overloaded the scrubber. An efficient scrubbing system large enough to handle all fumes would be necessary in any permanent setup. Water scrubbing would be satisfactory in corrosion-resistant equipment.

Reference to equations (a) and (b) above indicates that corrosion is an important problem. The use of iron or steel was preferred over an alloy, especially for intermittent service or if water was present. The following table (2, 4) gives corrosion rates for three metals in contact with FS.

Table 3

Corrosion Rated With FS

Metal	Continuous service	Intermittent service
	in./mo.	in./mo.
Iron	72×10^{-5}	200×10^{-5}
Steel	Negligible	30×10^{-5}
Monel	72×10^{-5}	$14,400 \times 10^{-5}$

For a permanent installation, the use of steel would be mandatory.

A polyvinyl chloride pipe was initially installed as a condenser vent line, but 50°C. the vapors were very corrosive, making immediate replacement necessary since the thermal plastic pipe began to sag badly.

V. CONCLUSIONS.

The process presented for thickening FS is satisfactory and can be scaled up, if the following important precautions are observed:

1. Use of only dry ammonium sulfate.

2. Use of an efficient exhaust scrubber.

VI. RECOMMENDATIONS.

None, since immediate requirements for thickened FS were met.

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